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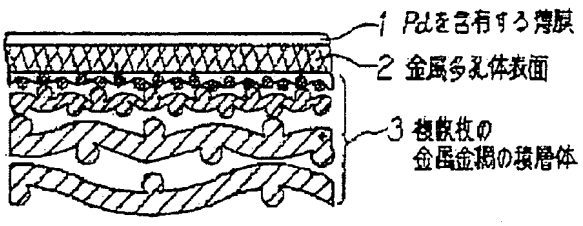
TITLE : PRODUCTION OF HYDROGEN SEPARATION MEMBRANE



ABSTRACT : PURPOSE: To obtain a hydrogen separation membrane having large hydrogen permeation amt. by drawing or blasting a metal porous body in the process of plating or ion plating on the surface of a thin film containing Pd of the metal porous body.

CONSTITUTION: A metal porous base body is produced by laminating and sintering a porous metal thin film 2 and plural numbers of metal nets 3 having small pores. The porous metal thin film 2 is obtd. by rolling and sintering a metal fiber nonwoven fabric having small fiber diameter (e.g. SUS 316L metal fiber nonwoven fabric having 2μm fiber diameter). The metal nets 3 are laminated in a various state according to the strength and dimension required to maintain the pressure-resistant strength. Then a thin film 1 containing Pd is formed on the surface of the porous metal thin film side by plating, ion plating, etc. In this process, the surface is subjected to drawing or blasting with metal in the stage that not all pores are sealed so that the pores not completely sealed is decreased in size. Then the thin film is treated by plating or ion plating till the thin film is completely sealed to obtain the hydrogen separation membrane.

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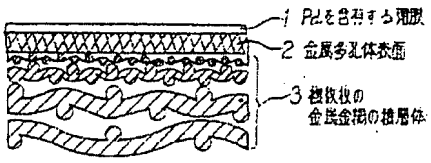
最終頁に続く

(54)【発明の名称】　水素分離膜の製造方法

(57)【要約】

【目的】　混合ガス中の水素を分離するための水素分離膜の製造方法に関する。

【構成】　細孔を有する金属多孔体の表面に、ＰｄまたはＰｄを含有する薄膜を形成させる方法において、めっきまたはイオンプレーティングなどの途中で封孔処理（金属などによりしごくか、ブラスト処理によって行う）を行う水素分離膜の製造方法。



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【特許請求の範囲】

【請求項1】　細孔を有する金属多孔体の表面に、Pdまたは Pdを含有する薄膜を形成させる方法において、めっきまたはイオンプレーティングなどの途中で封孔処理を行うことを特徴とする水素分離膜の製造方法。

【請求項2】　封孔処理を、PdまたはPdを含有する薄膜表面を金属などによりしごくかブラスト処理によって行うことを特徴とする請求項1記載の水素分離膜の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は混合ガス中の水素を分離するための水素分離膜の製造方法に関する。

【0002】

【従来の技術】省エネルギ型分離技術として、近年、膜による気体の分離法が注目を集めている。水素含有気体から水素を分離し、99．99％以上の高純度の水素を得る方法としてPdを主体とする膜を使用する方法が知られている。

【0003】従来はPd又はPdを主体とする合金を伸延し、薄膜とすることによって製造され、この膜は支持枠で支持して使用されていた。しかし、この方法は60～100μm程度の比較的厚いものを使用しなくてはならず、高価なPdの使用量が増大し、又水素の透過速度が小さい。

【0004】また、セラミックスなど無機質材料からなる多孔質体の表面にPdを含有する薄膜を形成させた水素分離膜が提案されているが、この水素分離膜は①脆性材料であり、機械的強度、振動・衝撃に弱いため、基材を破損しないように保持することが困難であり、特別な容器や支持法の設計を要する。②硬いため加工性が悪く長尺のパイプ状の成形体を得ることが難しいので設計の自由度も小さい。③溶接ができないため、シール部の構造が複雑になる。

【0005】さらに、また、セラミックスなど無機質材料に代わる0．1～20μmの細孔を有する多孔質金属体を基材とし、表面にPdを含有する薄膜を形成させた水素分離膜が提案されている。この多孔質金属多孔体の製造方法としては、①発泡（多孔質）金属をプレス成形し細孔径を制御したもの。②粒径の小さい金属微粉末（50μm以下）を焼結成形したもの。③化学反応により除去可能な粉末を金属粉末に混合又は溶融した金属に添加した後、粉末を化学反応により除去し細孔を生成させたものなどが提案されているが、何れも加工性が悪く薄肉で長尺のパイプを製造することが難しいので製造できるとしても耐圧強度を大きくするためには厚肉が必要で通気抵抗が大きくなり、水素分離膜の基材として適さない。

【0006】そこで、我々は、上記従来技術の問題点を解決する手段として、以下の方法により製作した水素分離膜を提案した。（特願平3～115811号）

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50μm以下のPdを含有する薄膜を容易に形成させるために繊維径の小さい金属繊維不織布を圧延、焼結することにより0．1～20μmと表面細孔が小さく、かつ通気抵抗を大きくしないために0．05～0．15㎜と薄肉とした多孔質金属薄膜と、耐圧強度を保持するために必要な強度・寸法に応じて積層状態を変えた100μm以上の細孔を有する複数枚の金網とを積層焼結した金属多孔体を製作する。この通気抵抗が小さく高い強度を有すると共に、長尺のパイプ曲げ加工などの加工が可能な金属多孔体の多孔質金属薄膜側表面に、（a）めっきなどの湿式のコーティング法、（b）真空蒸着法，イオンプレーティング、気相反応法（CVD）などのドライコーティング法により、Pdを含有する薄膜を薄く形成させた水素分離膜を製作する。この既提案の水素分離膜は溶接が可能なため、モジュール化が容易となる効果も有している。

【0007】

【発明が解決しようとする課題】Pd膜による水素の分離においても、通常の膜分離と同様に気体の透過速度は膜の厚さに逆比例する。したがって、水素透過速度の大きな水素分離膜を製作するにはPdを含有する薄膜をできる限り薄くすることが有効である。

【0008】しかし、Pdを含有する薄膜を形成させる方法として挙げられるめっきやイオンプレーティングにおいて、例えばPdを含有する薄膜を10μm以下に形成するためには金属多孔体の表面細孔径が最大でも10μm以下である必要があるが、既提案の金属多孔体は平均細孔径が5～7μmで最大15μm程度の表面細孔を有している。

【0009】したがって、現状の金属多孔体の表面細孔をめっきあるいはイオンプレーティングなどによりPdを含有する薄膜にて完全に封孔するためには多くの処理時間を要し、Pdを含有する薄膜の厚みが最低15～20μm必要である。その結果として水素透過速度が小さく、また、高価なPdの使用量が多くなるという問題がある。

【0010】また、水素透過速度の大きな水素分離膜とするためには金属多孔体そのものの通気抵抗が小さく開孔率の大きなことも必要であるが，表面細孔径を小さくすると通気抵抗が上昇し開孔率が低下するという問題がある。それを解決する手段としては非常に線径の細い金属繊維不織布を用いればよいが、焼結や加工条件が厳しくなり、また費用が多くかかるなどの問題がある。

【0011】本発明は上記技術水準に鑑み、通気抵抗が小さく、かつPd使用量も少なくてすむ水素分離膜の製造方法を提供しようとするものである。

【0012】

【課題を解決するための手段】本発明は

（1）細孔を有する金属多孔体の表面に、PdまたはP

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dを含有する薄膜を形成させる方法において、めっきまたはインプレーティングなどの途中で封孔処理を行うことを特徴とする水素分離膜の製造方法。

【0013】（2）封孔処理を、PdまたはPdを含有する薄膜表面を金属などによりしごくかブラスト処理によって行うことを特徴とする上記（1）記載の水素分離膜の製造方法。である。

【0014】本発明において封孔処理に当って、しごく材料として使用される金属はPdより硬さが大きい（ビッカース硬さ：Hv120以上）ものであればどのようなものでも使用でき、ブラスト処理材料はシリカ系のガラスビーズなどが使用される。ガラスビーズは球形であることが重要で、Pd膜を伸延するが削りとらない方がよい。また、鋼球のように質量が大きいものは金属多孔体を変形させるおそれがあるので好ましくない。

【0015】

【作用】以下、本発明を更に具体的に説明し、本発明の作用を併せて明らかにする。

【0016】（1）水素分離膜の基材として、繊維径の小さい金属繊維不織布を圧延、焼結して薄肉とした多孔質金属薄膜と、耐圧強度を保持するために必要な強度・寸法に応じて積層状態を変えた細孔を有する複数枚の金網とを積層焼結した金属多孔体を製作する。

【0017】（2）その金属多孔体の多孔質金属薄膜側表面にめっきあるいはイオンプレーティングなどによりPdを含有する薄膜を形成させる。

【0018】（3）完全に表明細孔を封孔するには最低15～20μm必要であるが、本発明では表面細孔が完全に封孔されていないめっきあるいはイオンプレーティングの途中段階において、Pdを含有する薄膜の表面を金属などによるしごきあるいはブラスト処理などを実施する。この処理によりPdを含有する薄膜の表面が潰れ完全に封孔していない開孔が小さくなる。

【0019】（4）その後、さらに表面細孔がPdを含有する薄膜にて完全に封孔するまでめっきあるいはイオンプレーティングなどの処理を行う。この処理はPdを含有する薄膜の表面細孔が小さくなっているため短時間で行うことができ、その結果として、非常に薄いPdを含有する薄膜をもつ水素分離膜の製造が可能となる。

【0020】

【実施例】

（実施例1）本発明の金属多孔体パイプにPdを含有する薄膜を形成させたものの断面構造の模式図を図1に示し、図1によって本発明の一実施例を説明する。

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【0021】線径2μmの多孔質金属薄膜となるSUS316L金属繊維不織布2と200、100、40メッシュの金網（SUS316）を重ねたもの3とを1200℃×3時間の条件で積層焼結した金属多孔体を巻き加工一溶接して20φ×300Lのパイプを製作した。このパイプの全厚みは約0．6㎜であり、多孔質金属薄膜の厚みは0．10㎜である。又、表面細孔径は平均で約6～7μm、開孔率は約30％であるが、最大15μmの細孔をある程度有している。この金属多孔体パイプ外表面の状況の走査型電子顕微鏡写真（1000倍）を図2に示す。

【0022】この金属多孔体パイプの外表面に、本発明を用いないで表面細孔が完全に封孔されるまで無電解めっき（Pdの化合物と還元剤を含有する液に浸漬）にてPdをめっきした。完全に封孔できるまでに要しためっき時間は20時間であり、Pdめっきの膜厚は約18μmであった。（比較例1）

【0023】また、同一条件の無電解めっきにて6時間めっき後の金属多孔体パイプの表面をガラスビーズによるブラスト処理（平均ビーズ径：115μm、圧力：5kg／cm²）を実施した。6時間めっき後のブラスト処理前後の通気抵抗測定結果を図3に、Pdめっき膜の表面状況の走査型電子顕微鏡写真（1000倍）を図4、図5に示す。ブラスト処理により表面の細孔が潰されて小さくなり、その結果通気抵抗が約200倍上昇している。

【0024】上記ブラスト処理後のパイプは、さらに4時間の同一条件の無電解めっきにて完全に封孔でき、そのPdめっきの膜1の厚さは約8．5μmであった。

（実施例1）

【0025】本発明を用いないでPdめっきしたもの（比較例1）及び本発明の方法でPdめっきしたもの（実施例1）の各々のパイプにつき、H_2混合ガスの圧力を3kg／cm² G、流量を200Nl／minで、500℃で実施した水素透過試験結果を表1に示す。

【0026】表1から明らかなように、本発明の方法によりPdめっきしたもの（実施例1）の水素透過速度は42cm³／cm²・minであり、本発明を用いない方法（比較例1）の2．1倍、従来のPdまたはPdを含有する合金を伸延したPd膜の約11倍である。

【表1】

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サンプル No.	Pdの膜厚	水素透過速度 (cm³ /cm² ・min)
実施例1	8．5μm	42
比較例1	18　μm	20
従来例	0．15mm (Pd－Ag膜)	3．4～4．1

(製品水素ガスは99．99%以上の純度)

【0027】また、本発明の方法（実施例1）でのPdめっき液の使用量は、本発明を用いない方法（比較例1）の半分であり、時間短縮のみでなく、費用節減からも効果がある。

【0028】（実施例2）実施例1で製作した図2に示す外表面を有する金属多孔体パイプの外表面に、本発明を用いないで表面細孔が完全に封孔されるまでイオンプレーティングを実施した。完全に封孔できるまでに要したイオンプレーティング時間は180分であり、Pdの膜厚は約25μmであった。（比較例2）

【0029】また、同一のイオンプレーティング条件にて50分イオンプレーティング後の金属多孔体パイプの表面を金属製の筆にてしごき処理を実施した。50分イオンプレーティング処理後のしごき処理前後の通気抵抗測定結果を図6に、Pdイオンプレーティング膜の表面状況の走査型電子顕微鏡写真（1000倍）を図7、図8に示す。しごき処理により表面の細孔が潰されて小さくなり、通気抵抗は約300倍上昇している。

*【0030】上記のしごき処理後のパイプは、さらに30分の同一条件のイオンプレーティング処理にて完全に封孔でき、そのPdイオンプレーティングの膜厚は約10μmであった。（実施例2）

【0031】本発明を用いないでイオンプレーティングしたもの（比較例2）及び本発明の方法でイオンプレーティングしたもの（実施例2）の各々のパイプにつき、H：混合ガスの圧力を3kg／cm² G、流量を20Nl／min で、500℃で実施した水素透過試験結果を表2に示す。

【0032】表2から明らかなように、本発明の方法によりイオンプレーティングしたもの（実施例2）の水素透過速度は34cm³ ／cm² ・min であり、本発明を用いない方法（比較例2）の約2．8倍、従来のPdまたはPdを含有する合金を伸延したPd膜の約8．5倍である。

【表2】

サンプル No.	Pdの膜厚	水素透過速度 (cm³ /cm² ・min)
実施例2	10　μm	34
比較例2	25　μm	12
従来例	0．15mm (Pd－Ag膜)	3．4～4．1

(製品水素ガスは99．99%以上の純度)

また、本発明の方法（実施例2）でのPdの使用量は、本発明を用いない方法（比較例2）の半分以下であり、時間短縮のみでなく、費用節減からも効果がある。

【0033】

【発明の効果】本発明によれば非常に薄いPdまたはPd合金膜を形成でき、水素透過量の大きい水素分離膜が提供でき、しかも作業時間の短縮および高価なPdの使用量も少なくてすむという利点がある。

【図面の簡単な説明】

【図1】本発明の金属多孔体パイプにPdを含有する薄膜を形成させたものの断面構造の模式図。

【図2】実施例1，2における金属多孔体パイプ外表面（めっき及びイオンプレーティング前）の微細金属組織を示す走査型電子顕微鏡写真。

【図3】実施例1における金属多孔体パイプへの6時間めっき後のブラスト処理前後の通気抵抗測定結果を示す図表。

【図4】実施例1における金属多孔体パイプへの6時間めっき後のブラスト処理前のPdめっき膜の表面状況の微細金属組織を示す走査型電子顕微鏡写真。

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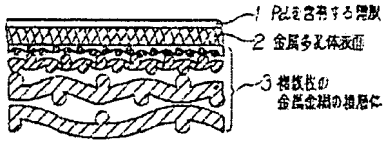
【図5】図4のPdめっき膜表面状況のものをブラスト処理した後のPdめっき膜の表面状況の微細金属組織を示す走査型電子顕微鏡写真。

【図6】実施例2における金属多孔体パイプへの50分イオンプレーティング処理後のしごき処理前後の通気抵抗測定結果を示す図表。

【図7】実施例2における金属多孔体パイプへの50分イオンプレーティング処理後のしごき処理前のPdイオンプレーティング膜の表面状況の微細金属組織を示す走査型電子顕微鏡写真。

【図8】図7のPdイオンプレーティング膜表面状況のものをしごき処理した後のPdイオンプレーティング表面状況の微細金属組織を示す走査型電子顕微鏡写真。

【図1】



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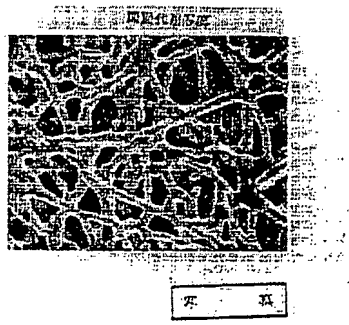

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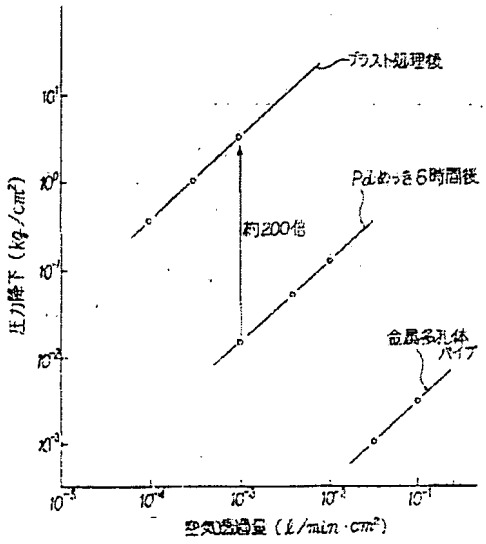

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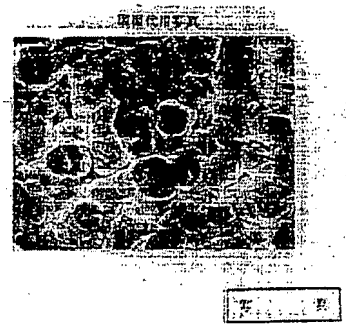

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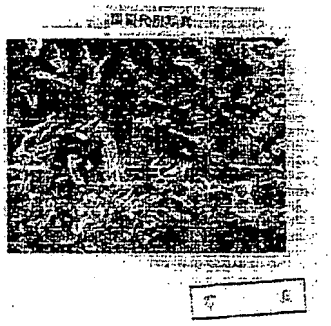

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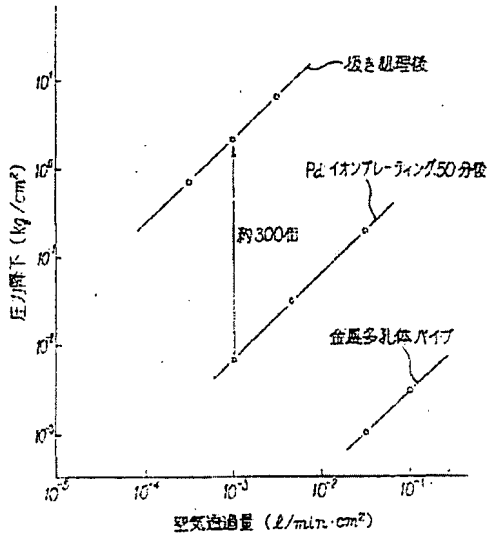
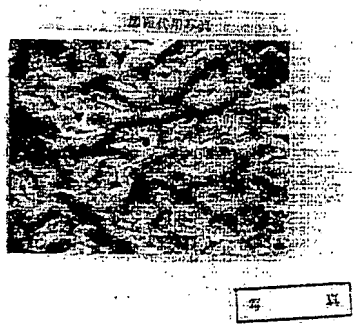
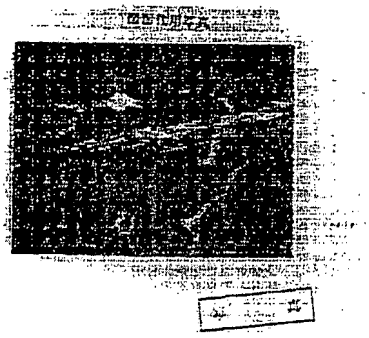


【図7】



【図8】



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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the manufacture approach of the hydrogen demarcation membrane for separating the hydrogen in mixed gas.
[0002]
[Description of the Prior Art] As energy-saving mold separation technology, the separation method of the gas by the film attracts attention in recent years. Hydrogen is separated from a hydrogen content gas and the approach of using the film which makes Pd a subject as an approach of obtaining the hydrogen of 99.99% or more of high grade is learned.
[0003] It was manufactured by carrying out the distraction of the alloy which makes Pd or Pd a subject, and considering as a thin film conventionally, and this film was supported and used by the housing. However, an about 60-100-micrometer comparatively thick thing must be used, and the amount of expensive Pd used increases, and this approach has the small transmission rate of hydrogen.
[0004] Moreover, although the hydrogen demarcation membrane which made the thin film containing Pd form in the front face of the porous body which consists of minerals ingredients, such as ceramics, is proposed, this hydrogen demarcation membrane is ** brittle material, since it is weak against a mechanical strength, and vibration and an impact, it is difficult to hold so that a base material may not be damaged, and it requires the design of a special container or the supporting method. ** Since it is hard and it difficult for workability to acquire the Plastic solid of the shape of a long pipe bad, the degree of freedom of a design is also small. ** Since welding is impossible, the structure of the seal section becomes complicated.
[0005] Furthermore, the porosity metal body which has the 0.1-20-micrometer pore replaced with minerals ingredients, such as ceramics, again is used as a base material, and the hydrogen demarcation membrane which made the thin film containing Pd form in a front face is proposed. It is what carried out press forming of the ** foaming (porosity) metal, and controlled pore size as the manufacture approach of this porosity metal porous body. ** What carried out sinter molding of the metal impalpable powder with a small particle size (50 micrometers or less). ** Although the thing which the chemical reaction removed [thing] powder and made pore generate is proposed after adding powder removable [with a chemical reaction] to the metal mixed or fused to metal powder, since it is difficult for all for workability to manufacture a long pipe with thin meat bad, though it can manufacture, in order to enlarge pressure resistance, thick meat is required, and ventilation resistance becomes large and is not suitable as a base material of a hydrogen demarcation membrane.
[0006] Then, we proposed the hydrogen demarcation membrane manufactured by the following approaches as a means to solve the trouble of the above-mentioned conventional technique. (Japanese Patent Application No. 3-No. 115811)
In order to make the thin film containing Pd 50 micrometers or less form easily, the small metal fiber nonwoven fabric of the diameter of fiber is rolled out. The porosity metal thin film used as 0.05-0.15mm and thin meat in order that 0.1-20 micrometers and surface pore might be small and might not enlarge ventilation resistance by sintering, The metal porous body which carried out laminating sintering of two or more wire gauzes which have the pore 100 micrometers or more which changed the laminating condition according to reinforcement and a dimension required in order to hold

pressure resistance is manufactured. While this ventilation resistance has small high reinforcement, the hydrogen demarcation membrane which made the thin film containing Pd form in the porosity metal thin film side front face of a metal porous body which can process long pipe bending etc. thinly by the dry coating methods, such as a coating method wet [, such as (a) plating,], (b) vacuum evaporation technique, ion plating, and vapor phase reaction (CVD), is manufactured. Since the hydrogen demarcation membrane proposed [this] can be welded, it also has the effectiveness that a modularization becomes easy.

[0007]

[Problem(s) to be Solved by the Invention] Also in separation of the hydrogen by Pd film, a gaseous transmission rate is inversely proportional to membranous thickness like the usual membrane separation. Therefore, it is effective in manufacturing a hydrogen demarcation membrane with a big hydrogen permeation rate to make the thin film containing Pd as thin as possible.

[0008] However, in the plating and ion plating which are mentioned as an approach of making the thin film containing Pd forming, although the surface pore size of a metal porous body needs to be 10 micrometers or less at the maximum in order to form the thin film containing Pd in 10 micrometers or less, as for the proposed metal porous body, average pore size has about 15 micrometers [a maximum of] surface pore by 5-7 micrometers.

[0009] Therefore, at least 15-20 micrometers of thickness of the thin film which requires many processing times in order to seal the surface pore of the present metal porous body completely with the thin film which contains Pd by plating or ion plating, and contains Pd are required. There is a problem that the amount of Pd used with it increases. [a small and hydrogen permeation rate and] [expensive as the result]

[0010] Moreover, in order to consider as a hydrogen demarcation membrane with a big hydrogen permeation rate, the ventilation resistance of the metal porous body itself is required also for the small big thing of hole density, but when surface pore size is made small, ventilation resistance goes up and there is a problem that hole density falls. Although what is necessary is just to use a metal fiber nonwoven fabric with a very thin wire size as a means to solve it, sintering and processing conditions become severe and there are problems, like costs cut in many.

[0011] In view of the above-mentioned technical level, ventilation resistance of this invention is small, and it is going to offer the manufacture approach of the hydrogen demarcation membrane which the amount of Pd used also has and ends. [few]

[0012]

[Means for Solving the Problem] This invention is the manufacture approach of the hydrogen demarcation membrane characterized by things for which sealing is performed in the middle of, such as plating or in plaiting, in the approach of making the thin film containing Pd or Pd forming in the front face of the metal porous body which has (1) pore.

[0013] (2) The manufacture approach of the hydrogen demarcation membrane the above-mentioned (1) publication characterized by drawing through with a metal etc. the thin film front face which contains Pd or Pd for sealing, or carrying out by blasting processing. It comes out.

[0014] If the metal used as an ingredient drawn through in sealing in this invention has hardness larger than Pd (Vickers hardness: 120 or more Hv(s)), anythings can be used and, as for a blasting processing ingredient, the glass bead of a silica system etc. will be used. It is better not to shave off, although it is important for a glass bead that it is a globular form and the distraction of the Pd film is carried out. Moreover, as a shot, since what has large mass has a possibility of making a metal porous body deforming, it is not so desirable.

[0015]

[Function] Hereafter, this invention is explained still more concretely, and an operation of this invention is combined and is clarified.

[0016] (1) Manufacture the metal porous body which carried out laminating sintering of two or more wire gauzes which have the porosity metal thin film which rolled out and sintered the small metal fiber nonwoven fabric of the diameter of fiber as a base material ~~of a~~ hydrogen demarcation membrane, and was used as thin meat, and the pore which changed the laminating condition according to reinforcement and a dimension required in order to hold pressure resistance.

[0017] (2) Make the thin film which contains Pd by plating or ion plating form in the porosity metal thin film side front face of the metal porous body.

[0018] (3) the plating with which sealing of the surface pore is not completely carried out in this

invention although at least 15-20 micrometers is required to seal manifestation pore completely, or ion plating – on the way – in a phase, the front face of the thin film containing Pd is depended on a metal etc. – carry out cover printing or blasting processing. Puncturing which the front face of the thin film which contains Pd by this processing collapses, and has not sealed completely becomes small.
[0019] (4) Process plating or ion plating until surface pore seals completely with the thin film containing Pd further after that. Since the surface pore of the thin film containing Pd is small, this processing can be performed in a short time, and the manufacture of a hydrogen demarcation membrane with the thin film which contains very thin Pd as that result of it is attained.
[0020]
[Example]
(Example 1) Although the thin film which contains Pd to the metal porous body pipe of this invention was made to form, the mimetic diagram of cross-section structure is shown in drawing 1 , and drawing 1 explains one example of this invention.
[0021] The metal porous body which carried out laminating sintering of the thing 3 which piled up the SUS316L metal fiber nonwoven fabrics 2 and 200 and the wire gauze (SUS316) of 100 or 40 meshes used as the porosity metal thin film of 2 micrometers of wire sizes on the conditions of 1200 degree-Cx 3 hours was rolled, it processed -> welded, and the pipe of 20phix300L was manufactured. The total thickness of this pipe is about 0.6mm, and the thickness of a porosity metal thin film is 0.10mm. Moreover, on the average, although surface pore size is about 6-7 micrometers and hole density is about 30%, it has 15 micrometers [a maximum of] pore to some extent. The scanning electron microscope photograph (1000 times) of the situation of this metal porous body pipe outside surface is shown in drawing 2 .
[0022] Pd was galvanized with nonelectrolytic plating (immersed in the liquid containing the compound and reducing agent of Pd) until sealing of the surface pore was completely carried out without using this invention for the outside surface of this metal porous body pipe. The plating time amount taken to be able to seal completely was 20 hours, and the thickness of Pd plating was about 18 micrometers. (Example 1 of a comparison)
[0023] Moreover, blasting processing (the diameter of an average bead: 115 micrometers and pressure:5 kg/cm2) according the front face of the metal porous body pipe after 6-hour plating to a glass bead was carried out with the nonelectrolytic plating of the same conditions. The ventilation resistance measurement result before and behind the blasting processing after 6-hour plating is shown in drawing 3 , and the scanning electron microscope photograph (1000 times) of the surface situation of Pd plating film is shown in drawing 4 and drawing 5 . Surface pore is crushed by blasting processing, it becomes small, and, as a result, ventilation resistance is going up about 200 times.
[0024] Being able to seal the pipe after the above-mentioned blasting processing completely with the nonelectrolytic plating of the same conditions of 4 more hours, the thickness of the film 1 of the Pd plating was about 8.5 micrometers. (Example 1)
[0025] It is attached to each pipe of what carried out Pd plating by the approach of the thing (example 1 of a comparison) which carried out Pd plating without using this invention, and this invention (example 1), and is H2. They are G and a flow rate 3kg/cm2 about the pressure of mixed gas 200 Nl/min The hydrogen permeation test result carried out at 500 degrees C is shown in Table 1.
[0026] the hydrogen permeation rate of what carried out Pd plating by the approach of this invention so that clearly from Table 1 (example 1) – 42cm3 / cm2, and min it is – it is 2.1 times of an approach (example 1 of a comparison) which does not use this invention, and about 11 times the Pd film which carried out the distraction of the alloy containing conventional Pd or Pd.
[Table 1]

サンプル No.	Pdの膜厚	水素透過速度 (cm³ /cm² ・min)
実施例1	8．5μm	42
比較例1	18 μm	20
従来例	0．15mm (Pd－Ag膜)	3．4～4．1

(製品水素ガスは99．99%以上の純度)

[0027] Moreover, the amount of Pd plating liquid used in the approach (example 1) of this invention is the one half of the approach (example 1 of a comparison) of not using this invention, and is effective not only from time amount compaction but cost saving.
[0028] (Example 2) Ion plating was carried out until sealing of the surface pore was completely carried out without using this invention for the outside surface of a metal porous body pipe which has the outside surface shown in drawing 2 manufactured in the example 1. The ion plating time amount taken to be able to seal completely was 180 minutes, and the thickness of Pd was about 25 micrometers. (Example 2 of a comparison)
[0029] Moreover, the front face of the metal porous body pipe after 50-minute ion plating was carried out on the same ion plating conditions, and cover-printing processing was carried out in metal **. The ventilation resistance measurement result before and behind the cover-printing processing after 50-minute ion plating processing is shown in drawing 6 , and the scanning electron microscope photograph (1000 times) of the surface situation of Pd ion plating film is shown in drawing 7 and drawing 8 . Surface pore is crushed by cover-printing processing, it becomes small, and ventilation resistance is going up about 300 times.
[0030] Being able to seal further the pipe after the above-mentioned cover-printing processing completely by ion plating processing of the same conditions for 30 minutes, the thickness of the Pd ion plating was about 10 micrometers. (Example 2)
[0031] It is attached to each pipe of what carried out ion plating by the approach of the thing (example 2 of a comparison) which carried out ion plating without using this invention, and this invention (example 2), and is H2. They are G and a flow rate 3kg/cm2 about the pressure of mixed gas 20 Nl/min The hydrogen permeation test result carried out at 500 degrees C is shown in Table 2.
[0032] the hydrogen permeation rate of what carried out ion plating by the approach of this invention so that clearly from Table 2 (example 2) – 34cm3 / cm2, and min it is – it is about 2.8 times of an approach (example 2 of a comparison) which does not use this invention, and about 8.5 times the Pd film which carried out the distraction of the alloy containing conventional Pd or Pd.
[Table 2]

サンプル No.	Pdの膜厚	水素透過速度 (cm³ /cm² ・min)
実施例2	10 μm	34
比較例2	25 μm	12
従来例	0．15mm (Pd－Ag膜)	3．4～4．1

(製品水素ガスは99．99%以上の純度)

Moreover, the amount of Pd used in the approach (example 2) of this invention is below one half of the approach (example 2 of a comparison) of not using this invention, and is effective not only from time amount compaction but cost saving.

[0033]
[Effect of the Invention] According to this invention, very thin Pd or Pd alloy film can be formed, a hydrogen demarcation membrane with the large amount of hydrogen permeation can be offered, and there is an advantage that there are also little compaction of working hours and amount of expensive Pd used, and moreover they end.

[Translation done.]

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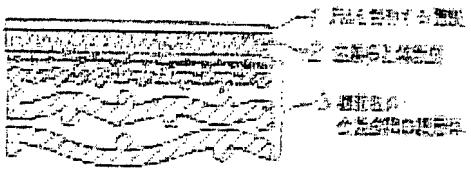
(54) [Title of the Invention] Method for production a hydrogen separation membrane

(57) [Abstract]

[Problems] The present invention relates to a method for producing a hydrogen separation membrane that separates out the hydrogen in a mixed gas.

[Means of Solution] A method for producing a hydrogen separation membrane, being a method for forming Pd or a thin film containing Pd on the surface of a metal porous body with fine pores, wherein the sealing of pores (either by drawing with metal, etc., or it is carried out by blasting) is carried out in the middle of plating or on plating.



1... Thin film containing Pd
2... Porous metal thin film
3... Laminated body with a plurality of metal nets

[Scope of Patent Claims]

[Claim 1] A method for producing a hydrogen separation membrane, being a method for forming Pd or a thin film containing Pd on the surface of a metal porous body with fine pores, wherein the sealing of the pores is carried out in the middle of plating or on plating.

[Claim 2] The method for producing a hydrogen separation membrane described in Claim 1, wherein the sealing of the pores is carried out either by drawing with metal, etc., or by blasting the Pd or the surface of a thin film containing Pd.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application] The present invention relates a method for producing a hydrogen separation membrane that separates out the hydrogen in a mixed gas.

[0002]

[Prior Art] Methods for separating gases by a membrane have attracted attention in recent years as an energy-saving separation technique. A method wherein a membrane whose main constituent is Pd is used is known of as a method for separating out the hydrogen from a hydrogen-containing gas, and obtaining hydrogen with a high purity of at least 99.99%.

[0003]

Conventionally, it is prepared by drawing Pd or an alloy whose main constituent is Pd, and making this into a thin film, and this membrane is supported in a support frame and used. However, in this method it is necessary to use relatively thick membranes about 60-100 μm thick, and the amount of expensive Pd increases and moreover the permeability rate of the hydrogen is small.

[0004]

In addition, a hydrogen separation membrane wherein a thin film containing Pd is formed on the surface of a porous body composed of a mineral material like ceramics, etc., has been proposed. However, this hydrogen membrane has the following drawbacks: ① It is a brittle material, and is weak when it comes to mechanical strength and vibration and shocks, so it is difficult to keep the base material so that it does not break, and a special container or the design of a support method are required. ② Since it is hard, its processing qualities are poor, and it is hard to obtain a long pipe-shaped molded body, so there is little degree of freedom in the design as well. ③ Since welding is not possible, the structure of the seal part is complicated.

[0005]

Moreover, a hydrogen separation membrane wherein a porous metal body that has fine pores 0.1-20 μm large in the place of the mineral material like ceramics, etc., is used as the base material, and a thin film containing Pd is formed on the surface has further been proposed. As methods for porous polypore metal, ① a method wherein foaming (porous) metal is press molded and the fine pore diameter is controlled, ② a method wherein a metal fine power with a small grain diameter (maximum of 50 μm) is formed by sintering, and ③ a method wherein a powder that can be eliminated by a chemical reaction is mixed with a metal powder or added to a molten metal, after which the powder is eliminated by a chemical reaction and fine pores are produced, have been proposed, but in all of these methods the processing qualities are poor, and it is hard to

prepare a long pipe with thin flesh, so even if its preparation is possible thick flesh is necessary to increase the compression strength and the air-flow resistance becomes greater, and it is not suitable as the base material of the hydrogen separation membrane.
[0006]

Accordingly, a hydrogen separation membrane prepared by the following method was proposed as a means for solving the above-mentioned problems of the prior art. (Japanese Patent Application No. H03[1991]-115811) In this method, there is prepared a polypore metal that laminates and sinters (a) a porous metal thin film whose surface fine ports are small at 0.1-20 μm due to the fact that metal fiber non-woven cloth with a small fiber diameter are stretched and sintered so that the a thin film containing a maximum of 50 μm Pd is formed easily, and that is made into a thin film of 0.05 to 0.15 mm so that the air-flow resistance does not increase, and (b) a plurality of metal nets with fine pore at least 100 μm large that alters the laminated state in accordance with the dimensions. In this method, there is prepared a hydrogen separation membrane whose air-flow resistance is small and that has high strength, and in addition a thin film containing Pd is formed thinly on the surface of a porous metal thin film of a polypore metal with which such processing as long pipe bending is possible, by (a) wet coating methods like plating, and (b) dry coating methods like vacuum deposition, ion plating, the gas-phase reaction method (CVD), etc. Since welding is possible with this previously proposed hydrogen separation membrane, it also has the effect that modularization is easy.
[0007]
[Problems that the Invention Attempts to Solve] In the separation of hydrogen by the Pd membrane, the permeability rate of gas is inversely proportional to the thickness of the membrane, just like ordinary membrane separation. Therefore, making the thin film containing Pd as thin as possible is effective in preparing a hydrogen separation membrane whose hydrogen permeability rate is large.
[0008]

However, in plating or ion plating, which have been cited as methods for forming a thin film containing Pd, it is necessary for the surface fine pore diameter of the polypore metal to be a maximum of 10 μm in order to form a thin film containing Pd 10 μm thick and under, but the previously proposed polypore metal has surface fine pores whose mean fine pore diameter is 5-7 μm and whose maximum fine pore diameter is about 15 μm.
[0009]

Therefore, a lot of processing time is required in order to seal completely the surface fine pores of current polypore metals with a thin film containing Pd by means of plating or ion plating, and it is necessary for the thickness of the thin film containing Pd to be a minimum of 15-20 μm. As a result of this, there are the problems that the hydrogen permeability rate is small, and the amount of expensive Pd used becomes greater.
[0010]

In addition, it is also necessary for the air-flow resistance of the polypore metal itself to be small and the open pore rate to be large in order to make a hydrogen separation membrane with a large hydrogen permeability rate, but there is the problem that when the surface fine pore diameter is reduced the air-flow resistance rises and the open pore rate declines. Metal fiber non-woven cloth with an extremely fine wire

diameter may be employed as the means for solving this problem, but there are such problems as the fact that the sintering or processing conditions become stringent, and in addition considerable expense is involved.

[0011]

The present invention attempts to provide a method for preparing a hydrogen separation membrane whose air-flow resistance is small, and wherein the amount of Pd used is small, in light of the above-mentioned technical level.

[0012]

[Means for Solving the Problems] The present invention is (1) method for producing a hydrogen separation membrane, being a method for forming Pd or a thin film containing Pd on the surface of a metal porous body with fine pores, wherein the sealing of the pores is carried out in the middle of plating or on plating.

[0013]

The present invention is (2) the method for producing a hydrogen separation membrane described in (1) above, wherein the sealing of the pores is carried out either by drawing with metal, etc., or by blasting the Pd or the surface of a thin film containing Pd.

[0014]

During the pore sealing in the present invention, it is possible to use anything for the metal used as the material that is drawn provided that it is something whose hardness (Vickers hardness) is greater than Pd, and silica glass beads, etc. are used for the blasting material. It is important that the glass beads be spherical, and although the Pd membrane is stretched it is best that it is not shaved off. In addition, like steel balls there is a risk that items with a large mass will deform the polypore metal, so this is not desirable.

[0015]

[Action] A more specific description of the present invention is provided below, and the action of the present invention is also clarified.

[0016]

(1) There is prepared a polypore metal that laminates and sinters (a) a porous metal thin film wherein a metal fiber non-woven cloth is stretched and sintered to make thin flesh, as the base material of the hydrogen separation membrane, and (b) a plurality of metal nets that have fine pores that alter the laminated state in accordance with the strength and dimensions required to maintain the compression strength.

[0017]

(2) A thin film containing Pd is formed on the surface of the porous metal thin film of this polypore metal by plating or ion plating.

[0018]

(3) A minimum size of 15-20 μm is required in order to seal completely the surface fine pores, but in the present invention drawing or blasting by metal, etc. are implemented for the surface of the thin film containing Pd, at the intermediate stage of the plating or ion plating when the surface fine pores have not been completely sealed. The surface of the thin film containing Pd collapses due to this treatment, and the open pores that have not been completely sealed become smaller.

[0019]

(4) After that, treatment like plating or ion plating is further carried out until the surface fine pores are completely sealed with the thin film containing Pd. It is possible to carry out this treatment in a short period of time since the surface fine pores of the thin

film have become smaller, and as a result of this it is possible to prepare a hydrogen separation membrane that has an extremely thin film containing Pd.
[0020]
[Embodiments]
(Embodiment 1) Figure 1 shows a pattern diagram of the sectional structure of an item wherein a thin film containing Pd is formed on the inventive polypore metal pipe. A description of one embodiment of the present invention is provided by means of Figure 1.
[0021]

Polypore metal that laminated and sintered at 1,200 degrees Centigrade for 3 hours SUS316L, a metal fiber non-woven cloth 2 that serves as the porous metal thin film with a wire diameter of 2 μm and an item wherein 200, 100 and 40 mesh metal nets (SUS316) are layered 3 is wound and welded to prepare a pipe of 20 ϕ x 300L. The full thickness of this pipe is approximately 0.6 mm, and the thickness of the porous metal thin film is 0.10 mm. In addition, the surface fine pore diameter is approximately 6-7 μm on average, and the open pore rate is approximately 30%, but it has fine pores with a maximum diameter of 15 μm to a certain extent. Figure 2 shows a scanning electron microscope photograph of the state of the outer surface of this polypore metal pipe.
[0022]

Pd was plated on the outer surface of this polypore metal pipe by non-electrolytic plating (immersed in a liquid containing a compound of Pd and a reducing agent) the surface fine pores were completely sealed without employing the present invention. The plating time required until these were completely sealed was 20 hours, and the membrane thickness of the Pd plating was approximately 18 μm. (Comparative Example 1)
[0023]

In addition, after 6 hours of plating by non-electrolytic plating under the same conditions, blasting by glass beads (mean bead diameter: 115 μm; pressure: 5 kg/cm^2) was carried out on the surface of the polypore metal pipe. Figure 3 shows the results of measurement of air-flow resistance before and after blasting following 6 hours of plating, and Figure 4 and Figure 5 show scanning electron microscope photographs (magnification of 1,000 times) of the state of the outer surface of the Pd plating membrane. The fine pores of the surface have collapsed due to the blasting and become smaller, and the air-flow resistance has risen by approximately 200 times.
[0024]

The pores of the pipe after the above-mentioned blasting were completely sealed by non-electrolytic plating under the same conditions for another 4 hours, and the thickness of the membrane 1 of that Pd plating was approximately 8.5 μm. (Embodiment 1)
[0025]

Table 1 shows the results of the hydrogen permeation test, which was conducted for the pipe that was Pd plated without employing the present invention (Comparative Example 1) and the pipe that was Pd plated with the method in the present invention (Embodiment 1), at 500 degrees Centigrade and conditions of 3 kg/cm^2 for the pressure of the H_2 mixed gas and 200N l/minute for the flow rate.
[0026]

As is clear from Table 1, the hydrogen permeability rate of the pipe that was Pd plated with the method in the present invention (Embodiment 1) is 42 cm^3/cm^2 • min, and

this is 2.1 times that of the method that does not employ the present invention (Comparative Example 1), and 11 times that of a conventional Pd membrane in which the Pd or an alloy containing Pd is stretched.

[Table 1]

Sample No.	Membrane thickness of the Pd	Hydrogen permeability rate (cm^3/cm^2 • min
Embodiment 1	8.5 μm	42
Comparative Example 1	18 μm	20
Conventional Example	0.15 mm (Pd-Ag membrane)	3.4-4.1

(The product hydrogen gas had a purity of at least 99.99%)

[0027]

In addition, the amount of the PD plating liquid use in the method of the present invention (Embodiment 1) is half that of the method that does not employ the present invention (Comparative Example 1), and thus there are effects not only in terms of shortening the time but also reducing expenses.

[0028]

(Embodiment 2) Ion plating was done on the outer surface of a polypore metal pipe with the surface shown in Figure 2 that was prepared in Embodiment 1 until the surface fine pores were completely sealed without employing the present invention. The ion plating time required until these were completely sealed was 180 minutes, and the membrane thickness of the Pd was approximately 25 μm. (Comparative Example 2)

[0029]

In addition, after 50 minutes hours of ion plating under the ion plating same conditions, drawing with a metal scraper was carried out on the surface of the polypore metal pipe. Figure 6 shows the results of measurement of air-flow resistance before and after drawing following 50 minutes of ion plating, and Figure 7 and Figure 8 show scanning electron microscope photographs (magnification of 1,000 times) of the state of the outer surface of the Pd ion plating membrane. The fine pores of the surface have collapsed due to the drawing and become smaller, and the air-flow resistance has risen by approximately 300 times.

[0024]

The pores of the pipe after the above-mentioned drawing were completely sealed by ion plating under the same conditions for another 30 minutes, and the thickness of the membrane 1 of that Pd plating was approximately 10 μm. (Embodiment 2)

[0031]

Table 1 shows the results of the hydrogen permeation test, which was conducted for the pipe that was ion plated without employing the present invention (Comparative Example 2) and the pipe that was ion plated with the method in the present invention (Embodiment 2), at 500 degrees Centigrade and conditions of 3 kg/cm^2 for the pressure of the H_2 mixed gas and 20N l/minute for the flow rate.

[0032]

As is clear from Table 2, the hydrogen permeability rate of the pipe that was ion plated with the method in the present invention (Embodiment 1) is 34 cm^3/cm^2 • min, and this is 2.8 times that of the method that does not employ the present invention

(Comparative Example 1), and 8.5 times that of a conventional Pd membrane in which the Pd or an alloy containing Pd is stretched.

[Table 2]

Sample No.	Membrane thickness of the Pd	Hydrogen permeability rate (cm^3/cm^2 • min
Embodiment 2	10 μm	34
Comparative Example 2	25 μm	12
Conventional Example	0.15 mm (Pd-Ag membrane)	3.4-4.1

(The product hydrogen gas had a purity of at least 99.99%)

In addition, the amount of the PD plating liquid use in the method of the present invention (Embodiment 2) is half that of the method that does not employ the present invention (Comparative Example 2), and thus there are effects not only in terms of shortening the time but also reducing expenses.

[0033]

[Effects of the Invention] According to the present invention, there are the advantages that it is possible to form an extremely thin Pd or Pd alloy membrane, and it is possible to provide a hydrogen permeable membrane with a large hydrogen permeability speed, and moreover it is possible to shorten the operation time and to use only a small amount of expensive Pd.

[Brief Description of the Invention]

[Figure 1] Figure 1 shows a pattern diagram of the sectional structure of an item wherein a thin film containing Pd is formed on the inventive polypore metal pipe.

[Figure 2] Figure 2 shows a scanning electron microscope photograph of the fine metal structure of the outer surface of this polypore metal pipe (before plating and ion plating) in Embodiments 1 and 2.

[Figure 3] Figure 3 shows the results of measurement of air-flow resistance before and after blasting following 6 hours of plating to the polypore metal pipe in Embodiment 1.

[Figure 4] Figure 4 shows a scanning electron microscope photograph of the fine metal structure of the state of the outer surface of the Pd plating membrane prior to blasting following 6 hours of plating to the polypore metal pipe in Embodiment 1.

[Figure 5] Figure 5 shows a scanning electron microscope photograph of the fine metal structure of the state of the outer surface of the Pd plating membrane after blasting of the item with the Pd plating membrane surface state shown in Figure 4.

[Figure 6] Figure 6 shows the results of measurement of air-flow resistance before and after drawing following 50 minutes of ion plating to the polypore metal pipe in Embodiment 2.

[Figure 7] Figure 7 shows a scanning electron microscope photograph of the fine metal structure of the state of the outer surface of the Pd ion plating membrane prior to drawing following 50 minutes of ion plating to the polypore metal pipe in Embodiment 2.

[Figure 8] Figure 8 shows a scanning electron microscope photograph of the fine metal structure of the state of the outer surface of the Pd ion plating membrane after blasting of the item with the Pd ion plating membrane surface state shown in Figure 7.

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[figure omitted]